STUDIES IN CRYSTAL AND MOLECULAR STRUCTURE.

PART.1.

DINITROGEN TETROXIDE.

PART.2.

β-SUCCINIC ACID.

THESIS.

Presented for the Degree of

Doctor of Philosophy

in the

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by

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PREFACE.

The work described in this thesis on the structure of dinitrogen tetroxide, and the experimental technique necessary to determine it, will soon be published in conjunction with Professor J. Monteath Robertson.

The first half of the experimental work on succinic acid, up to the point of obtaining the observed intensities, was done in conjunction with Dr. J. D. Morrison. The work when finished will be published in conjunction with Professor J. Monteath Robertson and Dr. J. D. Morrison.

I am indebted to Professor J. Monteath Robertson for suggesting the research problems, and for his constant assistance and encouragement throughout the work, and wish to offer him my sincere thanks. I would also like to thank the Department of Scientific and Industrial Research for a maintenance allowance, and Mr. R. Mc.Culloch for his assistance in building the apparatus required.

J. S. B.

August, 1950

SUMMARY

The thesis is divided into two distinct parts. The first deals with a low temperature technique which was developed to determine the molecular structure of dinitrogen tetroxide, and the subsequent determination of this structure. The X-ray diffraction intensities for planes in two zones of the dinitrogen tetroxide lattice have been obtained, and a structure for the molecule described which satisfies the observed results with a 16% discrepancy.

Part 2. describes the further refinement of the structure of succinic acid, by the Triple Fourier Series method. The method of obtaining accurate atomic co-ordinates from the summation totals is described in detail, and molecular dimensions resulting from the co-ordinates are reported.

In an appendix to the thesis some preliminary work on the crystal structure of azelaic acid is reported, with reference to previous work on the acid.

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STUDIES IN CRYSTAL AND MOLECULAR STRUCTURE.

PART 1. DINITROGEN TETROXIDE.

General Introduction:-

The molecular and crystal structure of dinitrogen tetroxide has not been previously determined accurately by X-ray measurements. Vegard (1931) has taken X-ray powder diffraction photographs of the gas crystallised in a camera specially built for the experiment, but owing to the limited information obtained from powder photographs , his results are not entirely satisfactory. Hendricks (1931) later showed that his results could be interpreted in a different fashion, but his suggestions are also inconclusive. The results of these two workers will be discussed later.

Because of the importance of dinitrogen tetroxide to both organic and inorganic chemistry, it was decided to make an attempt to study single crystals of this substance. The single crystal method of X-ray diffraction provides very accurate data for structure determination , which may lead to the complete elucidation of the structure being examined. However as dinitrogen tetroxide crystallises at -10°C and is a gas just above ordinary temperatures, it is obvious that the usual experimental methods used in the X-ray examination of single crystals are not applicable to this substance, and a new technique

has been developed. Although this new method was evolved primarily to study single crystals of N_2O_4, it could be made immediately applicable to all substances crystallising above -80°C. and with slight modifications, substances crystallising at much lower temperatures could be studied.

For convenience in presentation, Part 1. is divided into two sections (a) experimental technique, and (b) the crystal and molecular structure determination . The previous work on the molecule is discussed in the introduction to section (b).

PART 1. Section A.

Experimental Technique Developed for the Determination of the Crystal Structure of Dinitrogen Tetroxide at -40°C.

1.) Preparation of Crystals :-

Attempts to grow crystals of N_2O_4 by orthodox methods is made difficult not only by the low temperature of crystallisation, but also by its extreme reactivity, which limits the number of solvents which can be used. The gas or liquid dissolves without reaction in a few relatively inert solvents such as n-hexane or carbon tetrachloride, but in no case were suitable crystals obtained by cooling solutions saturated at room temperature.

Direct cooling of the liquid N_2O_4 by solid CO_2 in acetone or ether, did not give single crystals. The liquid usually supercooled and subsequently the whole mass instantaneously solidified. Direct cooling of only the surface of the liquid, in conjunction with nucleation was a little more successful. This method did produce single crystals, but they were developed only in two dimensions where they had grown along the surface of the liquid, and were quite useless for single crystal work.

By cooling from one end a fine bore ($\frac{1}{2}$m.m.) sealed glass capillary tube containing liquid N_2O_4, it was frequently found that the liquid solidified as a single crystal which grew from the cooled end. This method could be made more reliable, by first freezing the whole mass completely, and then slowly melting until only one or two small crystallites remained, after which the liquid was again cooled slowly and the temperature held a few degrees below the melting point. Under these conditions the liquid could be made to freeze almost invariably as a single crystal.

This method has been successfully used by American low temperature workers in the past, and is at present the method employed by Lipscomb and his colleagues in the University of Minnesota in Minneapolis.

Unfortunately, the axes of these crystals grown inside capillaries did not take up any preferred orientation relative to the axis of the tube, and this was a considerable disadvantage for the

following reasons. For complete crystallographic examination of a single crystal , it is important that it can be made to rotate in the X-ray beam with one of the crystal axes exactly coincident with the rotation axis. When the crystals being examined have well developed crystal faces, they can be set visually on an optical goniometer to rotate about a crystal axis. Single crystals however which have no definite shape or developed faces, must be set by trial. This may take considerable time, and in the early experiments with N_2O_4 crystals, it was important that a crystal could be mounted set and photographed, as quickly as possible. For this reason the crystals grown inside the capillaries were discarded in favour of crystals grown so that they had a reasonable shape, and at least a few crystal faces. The method of cooling the crystals while they were being photographed was gradually improved, so that latterly the time factor was not so important, and setting the crystals by trial could then be undertaken. However most of the work was done with crystals grown outside capillaries and this method of preparation was as follows.

Purified N_2O_4 gas from a cylinder, was allowed to pass slowly into a cooled receiver at such a velocity that single crystals of solid grew at the bottom and sides of the receiver in "stalactite" and "stalagmite" fashion. If the gas was passed into the receiver too quickly, a mass of fine downy and quite useless crystals were obtained. When the gas velocity was regulated by inspection of the receiver, the gas could be made to crystallise as quite large

crystals.

2.) Mounting the Crystals :-

Crystals for X-ray work are usually mounted on the spectrometer arcs by attaching the crystal with an adhesive, to a fine glass fibre attached to the arcs. This method could not be used with N_2O_4 because of the difficulty in finding a low temperature and unreactive adhesive, and because the high vapour pressure of the solid, even at low temperatures, made it imperative that the crystal be enclosed in some manner. These difficulties were overcome by sealing the crystal into a capillary tube which could be mounted on the arcs of the spectrometer.

A cold room was available for working at low temperatures, and the crystals were prepared in it. Unfortunately it could not be cooled below about -4°C. and this was still too warm to take the crystals out of the cooled receiver in which they were made. When needed, one of the crystals was removed and quickly placed on a metal platform cooled by solid CO_2. While the crystal was lying on this, it could be handled without melting, and was quickly inserted into a very thin walled glass capillary tube sealed at one end. The crystal was then pushed to the sealed end of the capillary by means of the glass fibre, which can be seen in fig. 1. then the capillary with the fibre projecting was inserted into a hole which had been drilled in a small block of solid CO_2. The open end of the capillary projecting from the block, was then sealed in a small gas flame, the solid CO_2 preventing the flame from melting the crystal. This is

shown diagrammatically, and the various dimensions are given in fig.1.

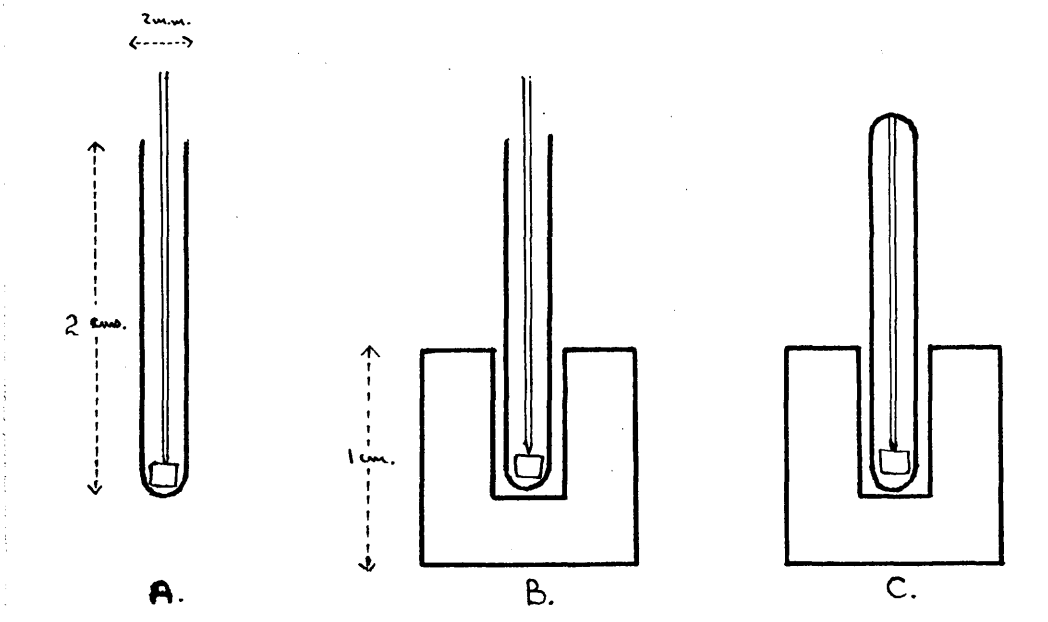


Fig. 1.

A.	B.	C.
Capillary tube with a crystal pushed to the sealed end by glass fibre.	Capillary inverted in a small block of solid carbon dioxide.	Open end of capillary sealed, glass fibre still holding crystal.

It was originally hoped that the capillaries used to enclose the crystals could be made from lithium borate glass, which is extremely pervious to X-rays. It was found however that the crystals react with this type of glass, especially if moisture is present, rendering it opaque to light almost immediately on contact. Extremely thin walled capillaries of ordinary soft glass were found to be

quite suitable. These were made thin walled by first blowing a bulb in a glass tube, and then drawing the capillaries from the bulb.

All work on the crystals and capillaries had to be done on top of the cooled platform, previously mentioned, and using forceps also cooled to a very low temperature, so that the heat of the hand was not conducted along the instrument for some time. This was done by keeping all the instruments used, in a flask of solid CO_2, and using only for a short time between each cooling.

Frost formation was a further difficulty. As the cooled platform, instruments, and the crystals themselves, were all cooled to about -70°C. they were much colder than the relatively warm cold room atmosphere at -4°C. Consequently the very considerable moisture still in the air tended to form frost on all these cooled surfaces. This was sufficiently prevented by working inside a glass cabinet, made from a balance case, the front of which was covered with a thick fabric with only two holes to admit the hands. The cabinet was sealed from the atmosphere as effectively as was possible, and a current of well dried oxygen or nitrogen from a cylinder, was passed in at such a velocity as to ensure that there was a small positive pressure of dry gas inside the cabinet. This excluded the moist cold room atmosphere, and prevented frost formation.

3) Setting the Crystal on the Spectrometer:-

The crystal in its sealed capillary, inserted in the block of solid CO_2, is quite safe even in a warm atmosphere, for as long as the CO_2 remains. It can be set on the spectrometer by fixing the end of the capillary projecting from

the block on to the arcs in the usual way,with plasticine. When this has been done, a cold air jet is fixed directly above the crystal , and the whole apparatus is positioned in front of the X-ray tube.

As the small block of CO_2 gradually disappears in the warm atmosphere of the laboratory, the capillary is slowly raised on the arcs into the end of the cold air tube, and the cold air stream is turned on. By the time that the CO_2 has completely gone the capillary and crystal are bathed in a stream of cold air , which is kept about $-40^{o}C$. Fig. 2. shows the cold air apparatus and spectrometer.

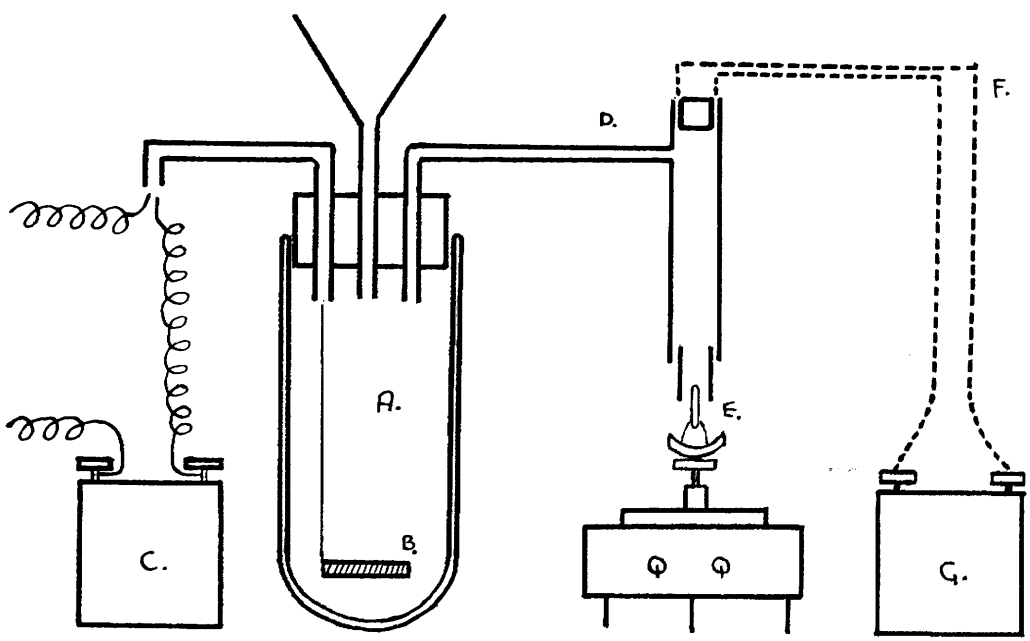


Fig. 2.

4.) Cold Air Apparatus:-

The stream of cold air is obtained by boiling liquid air (liquid oxygen usually used) in a vacuum flask A. by means of a nichrome heating element B. controlled by rheostat C. The air or oxygen boils off at about -180°C. and is led through a lagged glass tube D. to play on the capillary containing the crystal E. The temperature of the crystal can be controlled by varying the amount of air or oxygen boiling off, which is done by varying the rheostat. The temperature is measured by the thermocouple F. and galvanometer G. and the crystal is usually kept at -40 ± 1°C. while being set and photographed, as this was found to be the most convenient temperature at which to operate the apparatus.

It was mentioned above that the crystal was raised up into the end of the cold air tube, so that when the block of CO_2 had gone it would be completely bathed in the cold air stream. To enable the X-ray beam to reach the crystal while it is in the cold air stream, and so that the crystal may be seen to be set visually by reflections, the end of the cold air tube is constructed as shown in fig.3.

The lagged glass tube from the cold air apparatus has a smaller concentric tube B. made of copper, fixed inside at the bottom. This copper tube forms a constant temperature chamber for the end of the thermocouple C. The copper tube has a cellophane extension D. extending down to surround the capillary E. containing the crystal. This cellophane extension acts as a window pervious to both light and X-rays, while still protecting the crystal from the warm atmosphere.

Frost formation on this window is prevented by making the copper tube with its extension smaller than the lagged glass tube , with a space F. between it and the glass tube. This allows the perfectly dry cold air from the apparatus to pass down on both sides of the window, and prevents the moist atmosphere from reaching it.

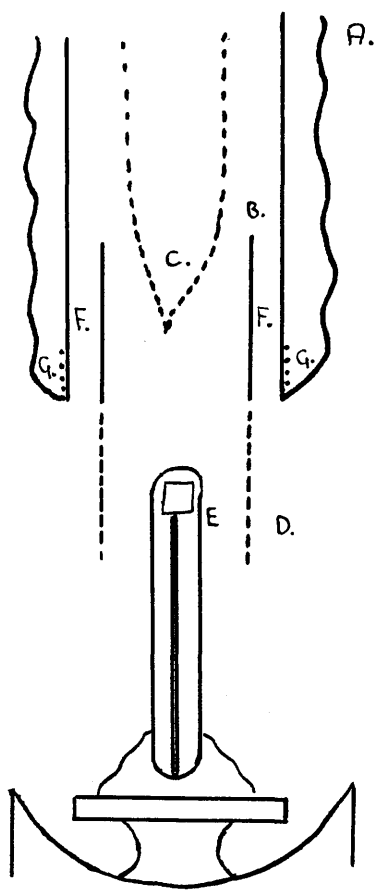


Fig.3.

It was also found that during long exposures, ice formation was liable to take place on the end of the lagged glass tube, and ice "stalactites" tended to grow down and cover the window. This was prevented by fitting a small nichrome heating element G to the end of the glass tube, which was arranged to give a temperature of just above $0^{\circ}C.$ at the end of the tube while the apparatus was in use. By operating this for about five minutes every half hour during a long exposure, ice formation could be effectively prevented, without appreciably heating the air issuing from the tube.

When the crystal had been set visually to rotate about a crystallographic axis, the camera was fitted to the spectrometer and a photograph taken. For the ordinary single crystal rotation photographs a special camera of 3cms. radius was made with a wide slit out of the side, this was used on the spectrometers in place of the usual completely cylindrical cameras. The wide slit allowed the camera to be fitted while the cold air tube was in position, and operating.

The moving film photographs taken with a horizontal type Weissenberg spectrometer, required a slightly different technique. The apparatus used was the same except that the cold air tube was arranged horizontally. The design of the instrument was such that screens and camera could be fitted without removing the cold air tube.

The life of the crystal if it survives the initial hazards of mounting and setting, depends on the length of time that the cold

air stream can be maintained. It was found that for the moving film photographs two liquid air flasks had to be fitted in parallel, so that they could be operated in succession, one always in use while the other was being recharged. By this method the crystals could be kept for as long as the supply of liquid air (or oxygen) lasted.

The apparatus employing only one flask, used for the short exposure rotation photographs, is shown in fig. 4. The X-ray tube can be seen in the background, and the arrangement of flask, spectrometer, and galvanometer can be clearly seen.

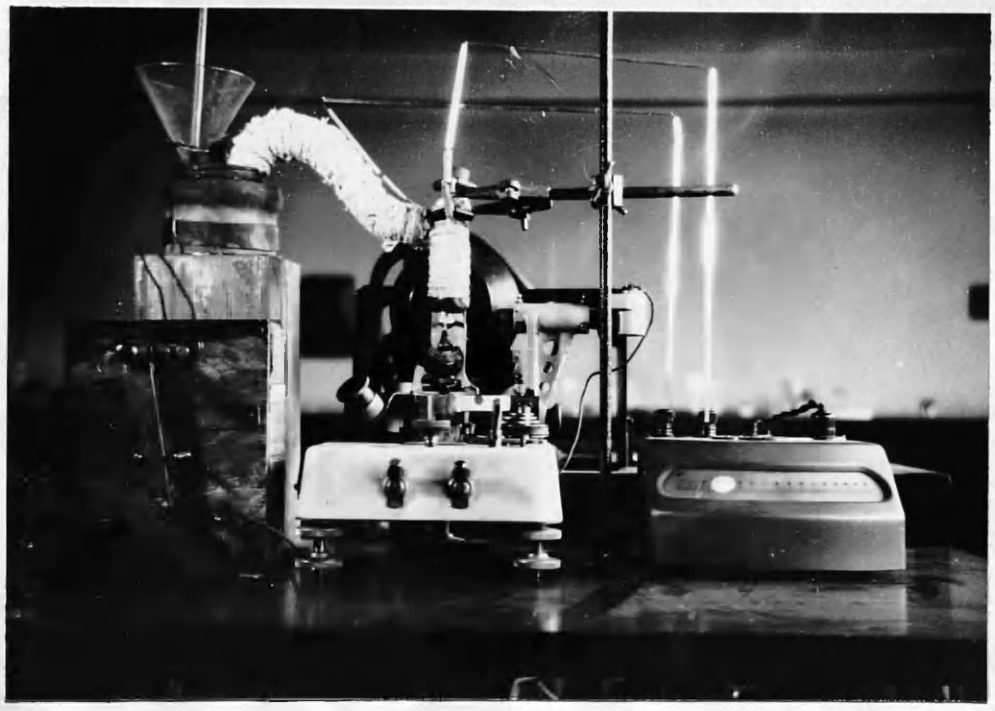


Fig. 4.

It was frequently found after a long exposure, that the crystal had decreased in size, and a slight powder deposit had built up on the inside walls of the tube. It was apparent that the crystal was subliming on to the walls of the capillary tube, even at the very low temperature at which it was maintained. This was presumably due to a slight temperature gradient between the walls of the capillary and the crystal at the centre, and although the effect of this must have been very small, it was eventually found to be the factor which determined the life of the crystal.

4.) Density of Solid Dinitrogen Tetroxide:-

As a necessary preliminary to the X-ray diffraction analysis of any substance, its density in the solid state must be found by ordinary physical methods. It was fortunate in the case of dinitrogen tetroxide that this is not required with a very high degree of accuracy, as there are more than the usual difficulties with this substance. In addition to the temperature difficulty, the solid either reacts with or is soluble in most of the usual liquids used for density determinations.

The method which was finally adopted, is a modification of the simple upthrust method. A quantity of the solid was first weighted in air then immersed in a liquid of known density. The whole determination had, of course, to be done in specially cooled apparatus, well below the melting point of the solid. A diagram of the apparatus is shown in fig. 5.

The liquid which was eventually found to be suitable as an

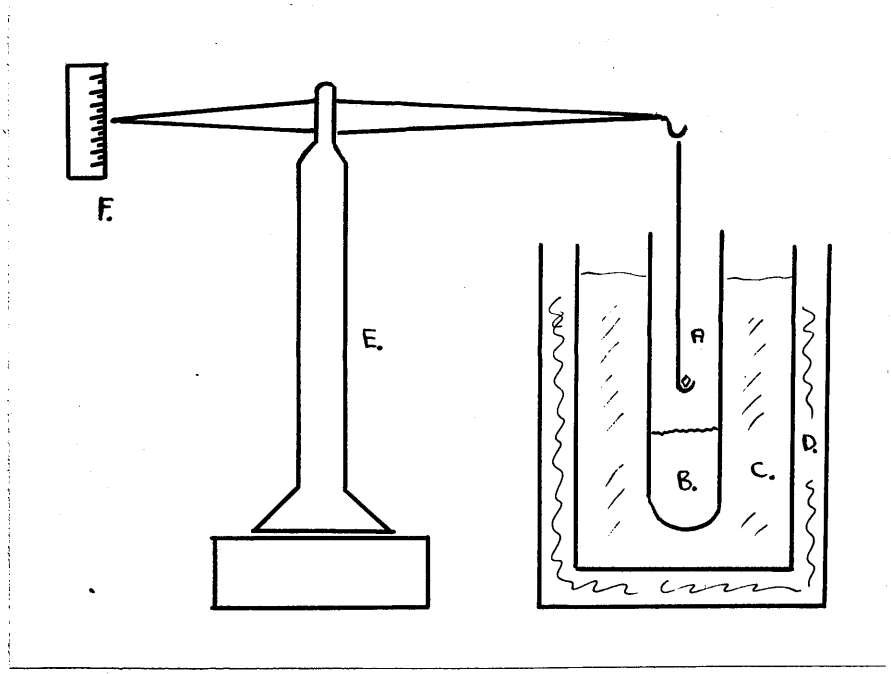


Fig.5.

immersion liquid, was a saturated solution of N_2O_4 in n-hexane. This was made by adding the pure liquid N_2O_4 to specially purified n-hexane, until no more was taken into solution. The dark brown solution which is obtained, fumes strongly at ordinary temperatures but can be comfortably used at $-20^{\circ}C$.

The method was as follows. Large crystals of N_2O_4 were made in the apparatus already described, and kept in the cooled receiver until required. When the temperature of the cooling mixture C, contained in the lagged vessel D. had been adjusted to $-20^{\circ}C$. a piece

of solid N_2O_4 was taken from the cooled receiver. This was put on the platinum stirrup A, and hung on the balance E, so that it was suspended just above the n-hexane solution B. As the balance was of the torsion wire type, the weight of the solid in air could be read directly from the calibrated scale F. The balance was then lowered so that the solid was completely immersed in the liquid, and its weight was again taken.

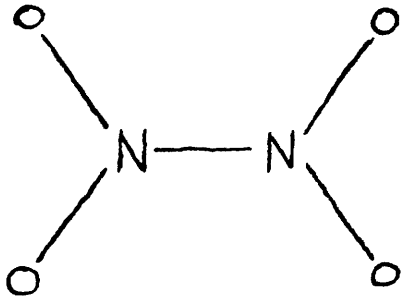
This was done several times with different weights of solid then the balance was removed, and the float of a Westphal balance immersed in the solution. This gave a direct reading of the density of the N_2O_4 /n-hexane solution which had been used as an immersion liquid, under the actual experimental conditions. After a correction had been applied for the volume of the wire stirrup immersed, a reasonably accurate measure of the density of the solid could be calculated. The average value obtained was $1.90 \pm .08$ grms./c.c. at $-20^{\circ}C$. This is in good agreement with the result obtained by Vegard (1931), who used an entirely different method.

PART 1. Section B.

The Crystal and Molecular Structure of Dinitrogen Tetroxide, determined at -40 degrees Centigrade.

Introduction :- The early X-ray work of Vegard (1931) and Hendricks (1931), with powder photographs of dinitrogen tetroxide did not satisfactorily elucidate the structure of the crystal. Vegard deduced from his measurements that the unit cell was cubic with "a"=7.77 A, and gave the space group as $(T_5);I2_13$. He showed that some agreement could be obtained between observed line intensities and those calculated assuming that 12 linear molecules of NO_2 were arranged in the unit cell with this spatial arrangement. The final positions in the unit cell which he chose for the atoms corresponded to a linear NO_2 molecule with N---O distance 1.38 A.

Hendricks subsequently suggested that Vegard's experimental data may be interpreted in a different way. He gave the space group as $(T_3);I23$, and assumed that six molecules of N_2O_4 were arranged in the unit cell. Hendricks did not attempt a rigorously quantitative interpretation of Vegard's results, but showed that the experimental data was consistent with the assumption that the structure of the molecule was approximately as follows,



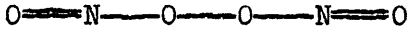
N---N distance between 1.10 and 1.70 A.

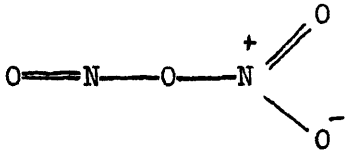
N---O distance About 1.20 A

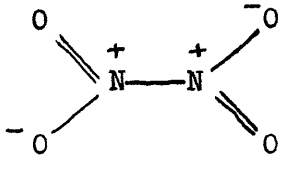
O--N--O angle about 120°.

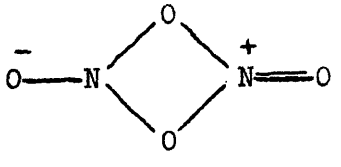
The planes of the two NO_2 groups were assumed to be inclined to each other at some angle between 0° and 25°.

Other physical methods of studying the structure of this molecule which have been tried, also provide limited information, and several structures have been suggested for the molecule in the past, these are as follows,

A. 

B. 

C. 

D. 

All the above structures are equally probable in the light of purely chemical evidence, and must be differentiated by a physical method. The infra red and Raman spectroscopic data (Sutherland 1933, Schaffert 1933, Harris and King 1934, Duchesne 1937.) indicates that the molecule is not linear and is symmetrical, which suggests

structures C or D. On the other hand structure C violates the adjacent charge rule, which has much evidence in its favour, and because of this Pauling suggested that structure B, was more likely. (Nature of the Chemical Bond.)

The spectroscopic data can only be satisfied by structure C, when it is assumed to be planar, with no free rotation about the N---N bond. As this bond appears to be about 1.6 A long, it did not seem likely that it would have much torsional rigidity. The structure D was suggested (Longuet-Higgins 1944) as an attempt to reconcile the apparently conflicting evidence, and it must be considered as equally probable.

The electron diffraction evidence is also inconclusive, (Maxwell, Mosley, and Deming 1934), but suggests that the N---N bond is 1.6 to 1.7 A long, the N---O bond about 1.15 A, with the angle between the NO_2 groups unknown.

On the whole the facts which emerge indicate, as does more recent chemical evidence (Ingold and Ingold 1947) that the most likely structure is that indicated as C, above. This present investigation into the structure, has shown that the single crystal X-ray diffraction data can best be satisfied by this form.

Crystal Data :-

Dinitrogen tetroxide, N_2O_4 ; M, 92.016 ; m.p. $-10^{\circ}C$; d, calc. 1.95, found 1.91 gm/cc. ; Body centred cubic, "a" = 7.74±.03A, from single crystal rotation measurements, "a" = 7.77±.01A, from powder diffraction measurements. Absent spectra (0kl) when k+l is odd, (hkl) when h+k+l is odd. Space group Im3, not determined uniquely by X-rays. Molecular symmetry, three two fold axes. m.m.m. Volume of unit cell 469.097 A^3. Total number of electrons in unit cell = F(000) = 276. The number of molecules in the unit cell Z = 6 .

Space Group :-

General reflections hkl were absent when h+k+l was odd. This condition is characteristic only of a body centered cell, and the space group was consequently indeterminate. The possible space groups were, I23, $I2_13$, Im3, or $I\bar{4}3m$, and from the point of view of systematic absences there was no method of differentiating between them.

It was found experimentally that the intensities of reflections of type $h\bar{k}\bar{l}$ and $h\bar{l}\bar{k}$ were not the same. These were measured on a Weissenberg film of the zero layer of the (111) diagonal axis. This shows that the crystal symmetry must be lower than that of the arrangement represented by $I\bar{4}3m$, which reduces the choice of space groups to three, of these only Im3 is a centrosymmetric arrangement, and as the molecule of dinitrogen tetroxide has been shown to have very high symmetry, this seemed the most likely space group.

Attempts to position planar molecules of the type represented by "C" and "D" in the introduction, in the space groups I23 or $I2_13$ invariably led to a centrosymmetric arrangement. It is possible and by no means unknown for a molecule of high symmetry to crystallise in a spatial configuration in which all its symmetry is not used, but it is exceptional. Consequently it seemed reasonable to assume as a first approximation, that the space group was Im3. Subsequent work showed that this assumption was justified, this being indeed the space group.

X-ray Measurements :-

All the X-ray work was carried out with copper K_α radiation (λ =1.54A) and photographic methods. The cell dimensions, space group etc., described in the above paragraph were determined by rotation, oscillation, and moving film photographs. Powder photographs were used to check the cell dimensions, which were estimated with an experimental divergence of .01A from the average figure quoted.

Intensities and Corrections :-

Intensities for planes in two zones of the N_2O_4 lattice were obtained from moving film records, by the multiple-film technique (Robertson 1943). Zero layer Weissenberg films about the (100) and (111) axes, gave planes

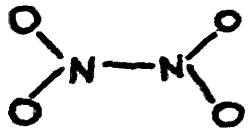
of type hho, hoo, and hko in the films about the principal axis, and of type $h\bar{h}o$ and $h\bar{k}\bar{l}$ on the diagonal zone. It was found that measurable intensities could be obtained for 70% and 76% of the possible reflecting planes in these two zones respectively.

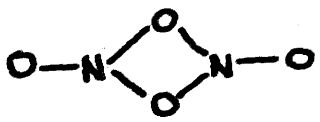
The crystals used were reasonably uniform in cross section, and it was not considered necessary to apply a factor to correct for the absorption of the beam in the crystal. The normal Lorentz and polarization factors were employed, and the observed structure factors were calculated from the intensities by the usual formula for mosaic type crystals. The final values chosen for structure factors of planes whose reflections appeared in both zones, were the average after correlation. As no absolute measurements of the observed intensities were available the structure factors could not be put on an absolute scale until final co-ordinates had been obtained for the atoms in the asymmetric unit.

Trial Structures:-

When a set of observed structure factor values (Fobs.) had been obtained for the principal zone of the crystal, the most likely structure was found by calculating structure factor values (Fcalc.), assuming the various possible types of molecule. The problem was complicated at this stage by the uncertainty of both the space group and the molecular structure. It was necessary to keep in mind, that if the molecule was not as symmetrical as had been assumed, then it was just as likely to fit into the space groups I23 or $I2_13$ as into Im3. The two molecular

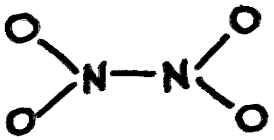
structures given the most attention, for reasons described earlier, were those represented by the following trial models,





Both these molecules display the same type of symmetry, viz m.m.m. and the space group Im3 has six special positions having this point symmetry. It seemed likely therefore, that either of these molecules might be situated in the crystal with its centre of symmetry on one of these special positions.

It was found by assuming bond lengths and angles for these two models, only the first of them, that is



give a reasonable interpretation of the observed intensities. After several trial structures, the discrepancy between F. calc. and F. obs. was reduced to under 30%, and this was taken as a reasonable indication that the assumptions made concerning the space group and molecular model were sufficiently good to justify refining the structure further.

Calculation of Structure Factors:-

For the space group Im3, the geometric structure factor equation is

$$A = 16\cos^2 2\pi.h/4+k/4+l/4 \; (\cos 2\pi hx \cos 2\pi ky \cos 2\pi lz + \cos 2\pi kx \cos 2\pi ly \cos 2\pi hz + \cos 2\pi lx \cos 2\pi hy \cos 2\pi kz)$$

A is the contribution of each atom in the asymmetric unit to the total reflection of any plane hkl. There are six molecules in the unit cell and 48 asymmetric units, this means that 1/8th. of the molecule is in the asymmetric unit, and this is equivalent to 1/2 of an oxygen atom and 1/4 of a nitrogen atom. Consequently since the structure factor S for any plane is obtained from the relationship

$$S = \Sigma A$$

then,

$$S = \tfrac{1}{4}A_n + \tfrac{1}{2}A_o$$

where A_n and A_o are the contributions from the nitrogen and oxygen atoms respectively.

The atomic numbers of oxygen and nitrogen atoms were sufficiently close to justify the use of an average atomic scattering curve, in conjunction with allowing for the greater scattering of the oxygen atom by multiplying its contribution to any plane by a numerical factor. As a first approximation to a true atomic scattering curve, for the purposes of trial structures an average theoretical curve was used. This was prepared from the data given in Internationale Tabellen Vol.2/

The effect of thermal vibration of the atoms is to modify the shape of this scattering curve, and as the N_2O_4 crystals were photographed relatively near to their melting point this may be of particular importance in this case. The data required to

approximately correct the curve for this temperature effect, was also found in Internationale Tabellen Vol.2.

When the structure and bond lengths of the molecule were finally known more accurately, an experimental temperature corrected scattering curve could be drawn from the data then available. This was found to agree very well with the theoretical curve, but for all the final structure factor calculations the experimental curve was used. The figures necessary to reproduce this curve are given in the following table.

Table,1.

"f" values for N_2O_4 at -40°C. including temperature factor.

$\sin\theta$ (λ=1.54A).....	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
"f"	100	99	76	48	36	28	20	15	11.5	9.5

Fourier Analysis:-

The agreement obtained between Fcalc. and Fobs. in the trial structures was considered to be sufficiently good to enable the structure to be finally refined by the Fourier projection method. The electron density ρ at any point x,y,z, is given by the series

$$\rho\,(x,y,z,) = \sum_{-\infty}^{+\infty}\sum\sum + \frac{|F(hkl)|}{V} \cos\left[2\pi hx/a + 2\pi ky/b + 2\pi lz/c - \alpha(HKL)\right]$$

In the case of the projection method, and assuming a centre of symmetry in the crystal,

$$\rho(x,y,) = \sum_{o}^{+\infty}\sum_{-}^{+} \frac{F(hk0)}{V} \cos\pi(hx/a + ky/b)$$

which for convenience in computation is best reduced to the form,

$$\rho(x,y,) = \sum\left[\sum K \cos h\theta_1\right]\cos k\theta_2 - \sum\left[\sum K \sin h\theta_1\right]\sin k\theta_2$$

where K is the coefficients, and θ_1 and θ_2 are $2\pi x/a$ and $2\pi y/b$ respectively.

In the case of a cubic unit cell the three axes are similar in all respects, consequently a projection of the electron density down any one of them is sufficient to give all the required parameters. The above series was evaluated over the area of the asymmetric unit of N_2O_4 which consisted of $\frac{1}{2}\times\frac{1}{4}$ of the cell edges. It is better, for convenience in presentation, to designate the three axes of the cell by different symbols in the usual manner. Consequently the planes used in the summation are indexed as if a projection were being done down the "c" axis of the cell, i.e. hk0 planes were used. Similarly in the tables of structure factors given later the planes of the principal zone are listed as hk0 planes.

For the projection, two axes were divided into 60 parts of 0.1295 A, and the summations were carried out by the three figure methods of J.M.Robertson (1948) and the results

were plotted on a scale of 10 cms. to one angstrom unit by graphical interpolation from the summation totals. The resulting electron density contour map , showing the positions finally assigned to the atom centres, is shown on fig. 6.

It was necessary to do two summations on the Fobs. values before the final structure shown on fig. 6. was obtained These were done on 64% of the possible reflections , and the final co-ordinates were all obtained from fully resolved atoms . It is difficult to identify individual atoms on the electron density plot and fig. 7. shows diagrammatically the positions of the various atoms, labelled O (oxygen) and N (nitrogen) when projected on to the base of the unit cell. The area of the base of the asymmetric unit is marked by the dotted line.

Atomic Co-ordinates:-

The co-ordinates of the two atoms of the asymmetric unit , are as follows , centre of symmetry as origin

.....	xA.	yA.	zA.	$2\pi x/a.$	$2\pi y/a.$	$2\pi z/a.$
N.....	3.06	0.0	0.0	141.8	0.0	0.0
O.....	2.53	1.04	0.0	117.4	48.2	0.0

In the unit cell the 12 nitrogen atoms occupy the 12 special positions of the space group, i.e.

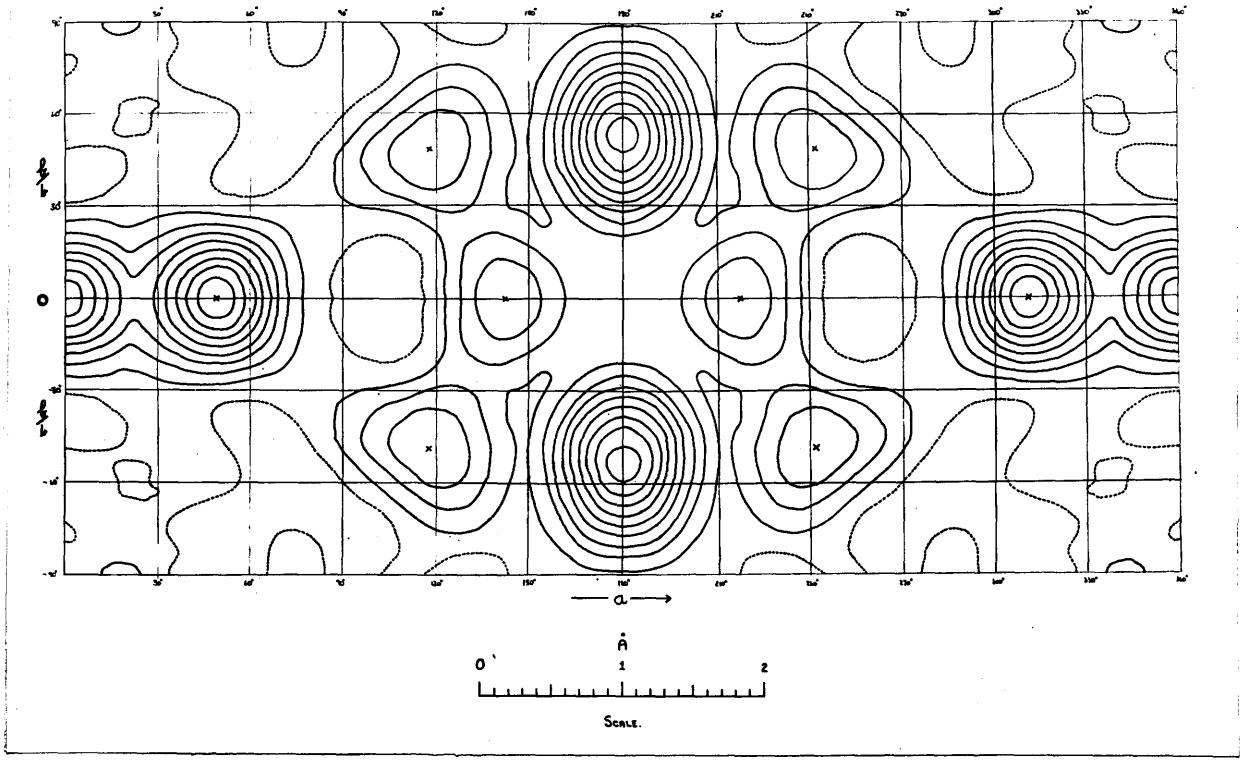


Fig.6.

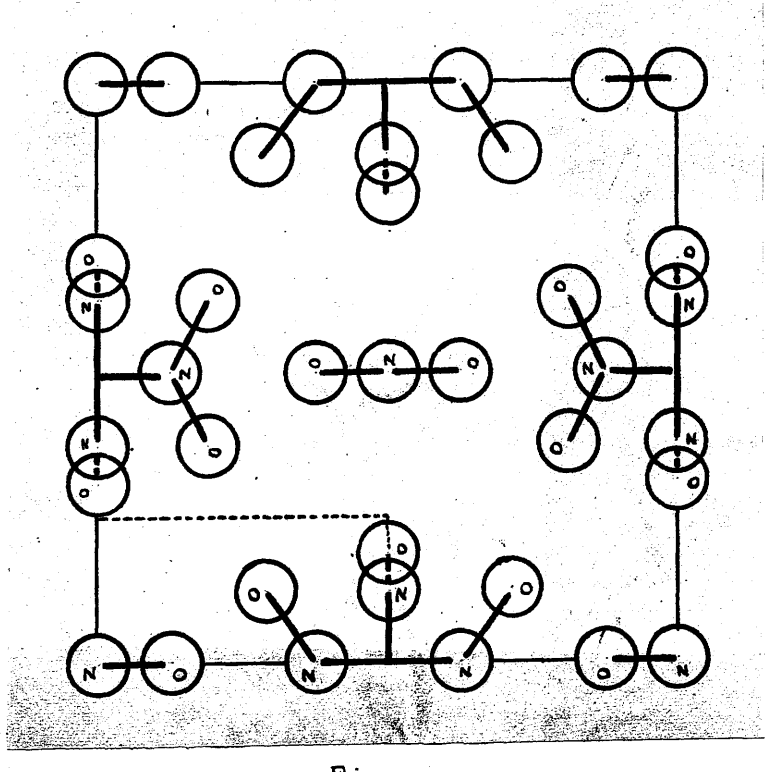


Fig.7.

Special positions of the space group,

ooo $\frac{111}{222}$ +

(xoo, oxo, oox, $\bar{x}$oo, o$\bar{x}$o, oo$\bar{x}$,)

and the 24 oxygen atoms are in the 24 special positions of the space group,

ooo $\frac{111}{222}$ +

(oyz, zoy, yzo, o$\bar{y}\bar{z}$, $\bar{z}$o$\bar{y}$, $\bar{y}\bar{z}$o,

oy$\bar{z}$, $\bar{z}$oy, y$\bar{z}$o, o$\bar{y}$z, zo$\bar{y}$, $\bar{y}$zo,)

where,

x = 3.06 A

y = 2.53 A

z = 1.04 A

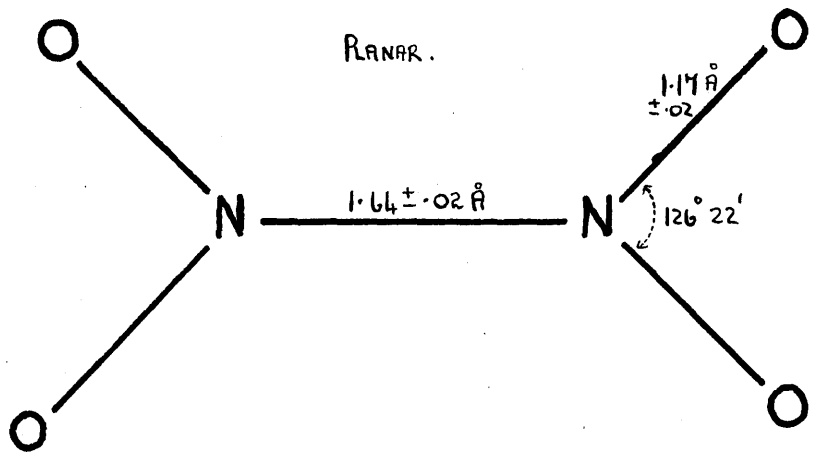
These final co-ordinates , when used to calculate new structure factors were found to give no further sign changes, and the discrepancy between Fcalc. and Fobs. estimated from the expression,

$$\text{discrep.}\Delta = \frac{\sum (|\text{Fobs.}| - |\text{Fcalc.}|) \times 100}{\sum |\text{Fobs.}|}$$

was 15.9% for the principal zone and 16.4% for the (111) diagonal zone, with an overall value of approximately 16%. It is probable that these values may be slightly improved if a separate scattering curve was used for oxygen and nitrogen atoms. The values for the observed and calculated structure factors are shown in table 2.

Dimensions of the Molecule:-

From the electron density contour map the various bond lengths of the molecule could be measured directly. These were found to be as shown in the following diagram



Fig, 8.

Intermolecular Distances:-

The positions of the N_2O_4 molecules relative to the unit cell axes are shown in fig. 9. If 0 is taken as the origin of the cell , there is a molecule with its centre of symmetry at the centre of every cell edge, and also at the centre of every cell face. The planes of the molecules at the cell edges are at right angles to the planes of those on the cell faces, and the planes of the molecules at the cell edges are in the planes of the cell faces. The molecules labelled 1, 2, and 3, in fig. 9 are related to each other by the operation of the three-fold axis of the space

group, which is along the (111) diagonal of the cell. The other molecules in the cell can be positioned from any one of these and the operation of the space group symmetry elements.

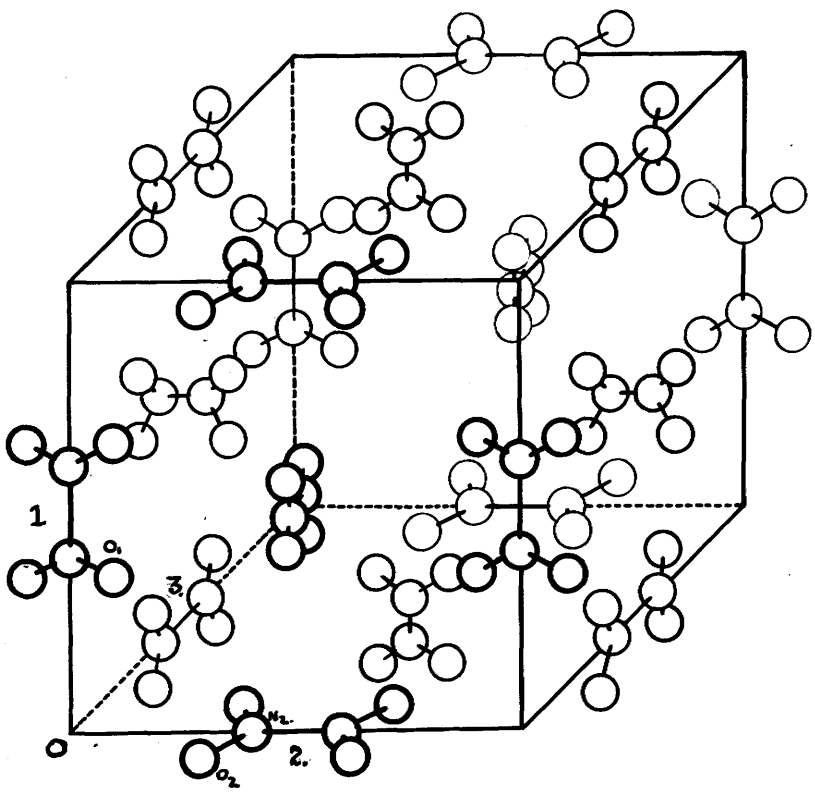


Fig.9

The distances between the atoms of different molecules was found to be as follows, where the subscript figures represent the atoms as shown in fig. 9.

$O_1 \ldots\ldots O_2$ 3.12 A

$O_1 \ldots\ldots N_2$ 3.24 A

These being the closest approaches.

The van der Waal's radii usually given for oxygen and nitrogen atoms are,

N = 1.5±.1 A.

O = 1.4±.1 A. (Nature of the Chemical Bond, Pauling.)

Consequently the distances found for N_2O_4 seem to be a little greater than usual. The high vapour pressure of the solid would seem to indicate that the intermolecular forces are relatively weak, and the large van der Waal's distances are consequently in keeping with the general physical properties of the solid.

Discussion :-

Neither Vegard (1931) nor Hendricks (1931) gave accurate bond measurements for the molecule of dinitrogen tetroxide, so that the present results cannot be compared to previous crystal measurements. The values predicted by other physical methods however, are in good general agreement with the present work. Even the very long N----N bond is not unexpected as previous data had suggested that it would be in the region of 1.6 A long. If the N----N bond length of 1.47 A, as found in hydrazine is taken as the length of the single bond, then the distance of 1.64 A. found in N_2O_4, shows that the N----N

link has much less than single bond character.

Since the nitrogen atoms have only one parameter which is variable, the effect of the length of this bond on the discrepancy between the observed and calculated structure factors can easily be estimated. Values of this parameter were chosen corresponding to a variation in the length of this N----N bond between 1.40 and 1.88 A; structure factors were calculated, and the discrepancy expressed in the usual way over a representative number of planes. This discrepancy was then plotted against bond length, and the curve obtained is shown in fig. 10.

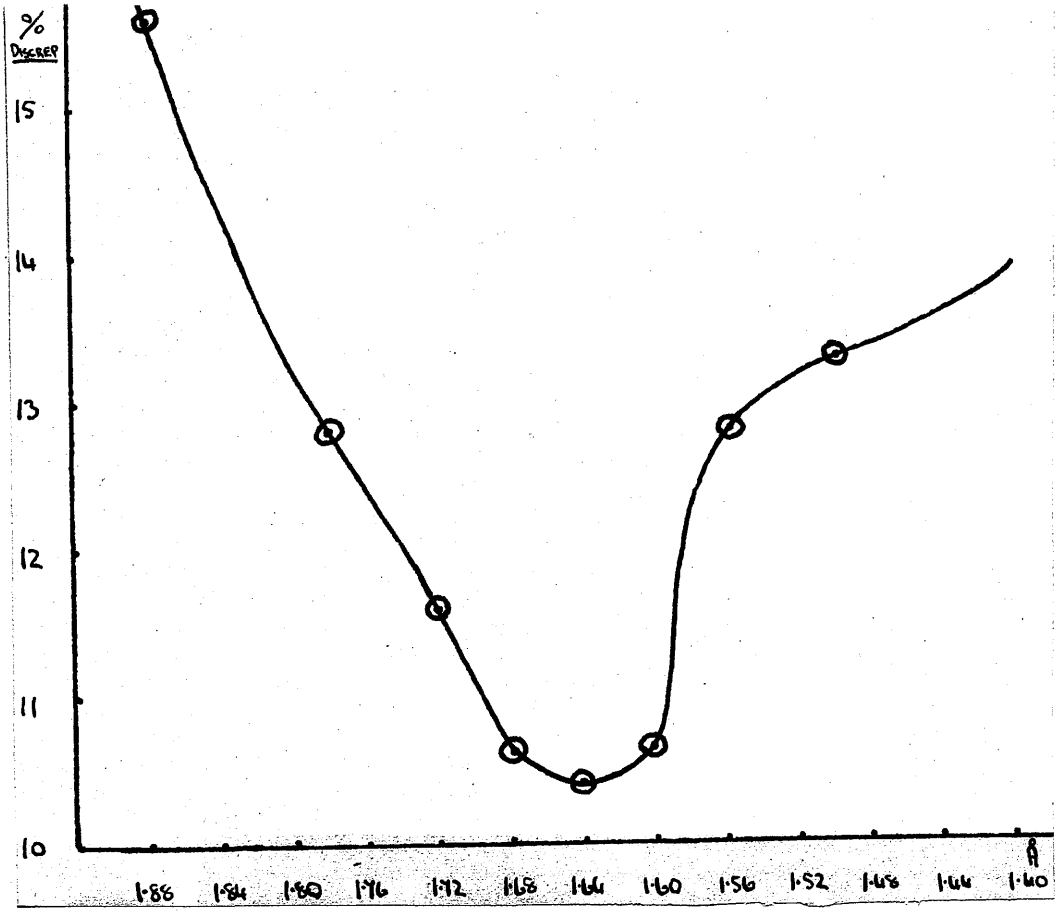


Fig.10.

It can be seen that the curve has a sharp minimum at a distance corresponding to an N----N bond length of 1.64 A. The N----O bond length found to be 1.17 A is slightly greater than the value of 1.16 A usually given for the N----O double bond, and agrees very well with the values predicted. It should be noticed , that it is hardly significantly different from the value predicted for the N----O bond in the NO_2 molecule (Pauling, The Nature of the Chemical Bond), this is a further indication that the N----N link is extremely weak.

The value of the O---N---O angle has been variously reported between 116° and 140° , the spectroscopic data (Sutherland 1933, Duchesne 1937, Schaffert 1933, Harris and King 1934.) suggests an angle of about 120°, while entropy measurements (Giauque and Kemp 1938.) favour a higher value of about 133°. In general it can be said that the value of 126° found in this investigation is in agreement with previous work.

Table 2.

Observed and Calculated values of the Structure Factors for N_2O_4 .

hkl.	sinθ.	Fobs.	Fcalc.	hkl.	sinθ.	Fobs.	Fcalc.
200	0.197	193.5	+203.0	350	0.577	32.3	- 62.2
400	0.397	<18.8	+ 7.1	370	0.757	<26.9	+ 12.7
600	0.595	126.5	+141.5	390	0.940	<16.2	+ 12.7
800	0.794	59.2	+ 62.1	420	0.442	99.5	-114.5
10,00	0.991	32.2	+ 34.0	460	0.716	32.2	- 9.9
110	0.139	65.9	- 69.2	480	0.889	40.9	- 43.9
220	0.279	13.4	- 11.4	510	0.505	59.2	- 66.4
330	0.418	<18.8	- 5.7	530	0.577	119.5	+107.5
440	0.558	84.6	- 68.0	570	0.856	22.9	- 15.6
550	0.697	35.0	+ 8.5	620	0.629	<25.6	- 5.7
660	0.842	37.7	+ 39.7	640	0.716	35.0	- 41.1
770	0.986	26.8	+ 22.7	710	0.702	<26.9	+ 15.6
130	0.312	252.0	+265.0	730	0.756	72.7	+ 83.6
150	0.505	65.8	+ 42.5	750	0.856	22.9	+ 25.5
170	0.702	<26.9	+ 5.7	820	0.815	40.3	+ 29.7
190	0.897	<22.8	+ 28.2	840	0.889	<21.5	+ 36.7
240	0.442	22.9	+ 19.9	860	0.992	28.2	+ 46.7
260	0.629	55.1	+ 42.5	910	0.897	<22.8	+ 4.2
280	0.819	<25.6	- 24.1	930	0.940	<16.2	+ 15.6
310	0.312	47.0	- 45.3	$2\bar{1}\bar{1}$	0.244	140.5	-161.5

Table 2. cont.

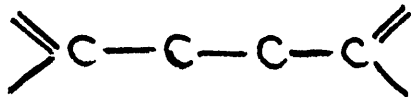
hkl.	sinθ.	Fobs.	Fcalc.	hkl.	sinθ.	Fobs.	Fcalc.
$4\bar{2}\bar{2}$	0.487	35.7	+ 36.8	$6\bar{1}\bar{5}$	0.779	< 17.4	+ 12.7
$6\bar{3}\bar{3}$	0.727	30.5	- 41.1	$7\bar{2}\bar{5}$	0.877	< 14.0	+ 2.8
$8\bar{4}\bar{4}$	0.972	15.6	+ 8.5	$8\bar{3}\bar{5}$	0.979	< 8.5	+ 5.7
$3\bar{2}\bar{1}$	0.372	< 11.4	- 1.4	$7\bar{1}\bar{6}$	0.918	< 12.2	+ 2.8
$4\bar{3}\bar{1}$	0.505	65.1	+ 63.7				
$5\bar{4}\bar{1}$	0.641	24.3	+ 18.4				
$6\bar{5}\bar{1}$	0.779	33.2	- 36.8				
$7\bar{6}\bar{1}$	0.918	21.8	- 8.5				
$3\bar{1}\bar{2}$	0.372	104.5	+111.5				
$5\bar{3}\bar{2}$	0.610	51.2	+ 63.7				
$6\bar{4}\bar{2}$	0.742	44.4	- 52.2				
$7\bar{5}\bar{2}$	0.877	< 14.0	+ 2.8				
$4\bar{1}\bar{3}$	0.505	76.8	- 86.2				
$5\bar{2}\bar{3}$	0.610	37.4	+ 29.8				
$7\bar{4}\bar{3}$	0.852	38.3	+ 32.6				
$8\bar{5}\bar{3}$	0.979	59.0	+ 59.2				
$5\bar{1}\bar{4}$	0.641	17.4	- 5.7				
$6\bar{2}\bar{4}$	0.742	< 17.4	- 4.2				
$7\bar{3}\bar{4}$	0.852	32.2	- 32.6				

STUDIES IN CRYSTAL AND MOLECULAR STRUCTURE

PART 2. SUCCINIC ACID, INVESTIGATED BY THE TRIPLE FOURIER SERIES METHOD.

Introduction:-

The dicarboxylic acids form a well defined series of crystalline compounds, and the crystal and molecular structures of a number of them have been determined by the usual two dimensional Fourier methods. The structure of succinic acid has been determined by Verweel and Macgillavry (1938, 1939.) and later more accurately Morrison and Robertson (1949). The results of both these investigations are in good general agreement, although the fine structure of the molecule as reported by Morrison and Robertson shows some interesting features not found by the earlier workers. The central C----C bond for example, appeared to be slightly shorter than normal, which suggested that there may be some interaction between this bond and the carboxyl groups. Although this contraction was just on the limits of experimental error as measured, other considerations made it appear significant. The environment of the central C----C bond in succinic acid is very similar to that in dibenzyl and to the carbon bond in geranylamine hydrochloride situated centrally between the ethylene linkages. In all cases the structure is of the type,



and in the case of dibenzyl and geranylamine hydrochloride, (Jeffrey, 1947. Cox and Cruickshank, 1948) a notable contraction from the normal C-----C single bond length of 1.54 A has been observed.

The electron density contour map of the "a" axis projection of succinic acid shows small peaks in the two electron contour levels which correspond approximately to the positions of the hydrogen atoms of the CH_2 groups. This is shown in fig. 11.

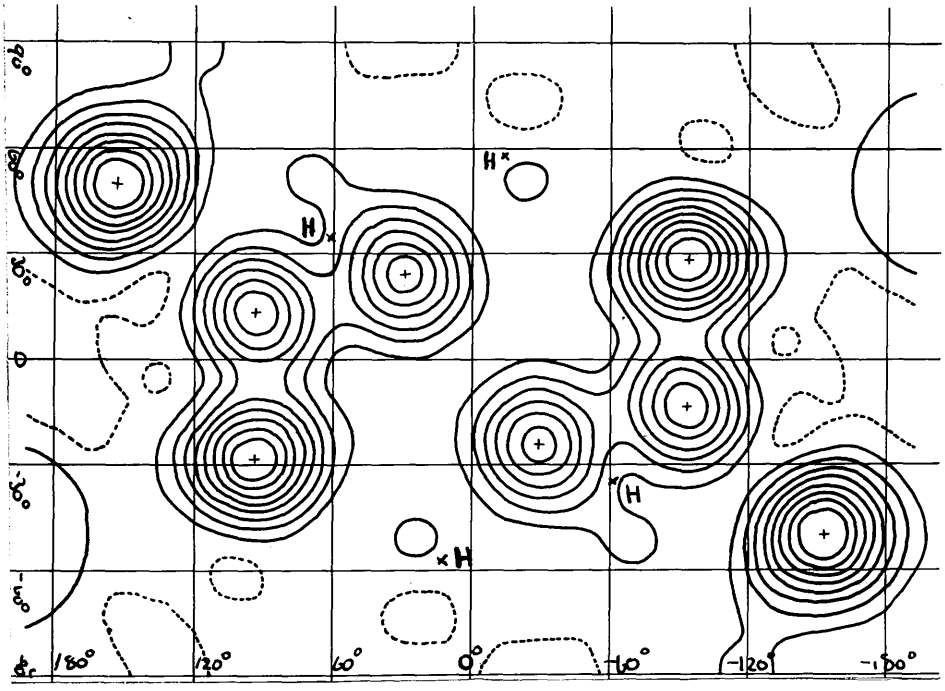


Fig.11.

Contour map for "a" axis projection of succinic acid, showing positions assigned to atoms of hydrogen assuming normal bond lengths and angles.

Hydrogen atoms are not usually resolved by the Fourier method, and it is of considerable interest that these small peaks should appear. Although it is by no means certain that they are due to hydrogen atoms, it is interesting to note that a similar suggestion of hydrogen atoms was found in naphthalene, (Abrahams, Robertson, and White, 1949). In this latter case the evidence was much more conclusive, as the structure had been determined very accurately by three dimensional methods.

The present investigation is concerned with the redetermination of the succinic acid structure, using all the X-ray reflections within the range of copper K_α radiation (λ =1.54 A). From a possible of 585 structure factors, 455 have been observed. This represents 77.8% of the total. The preliminary two dimensional projections gave sufficiently accurate atomic co-ordinates to assign reliable phase constants to 442 of these structure factors. These measurements were then used in the new structure determination by the triple Fourier series method.

Crystal Data :-

β-Succinic acid, $C_4H_6O_4$; M,= 118.1 ; m.p. 185° ; d, calc. 1.561, found 1.550. Monoclinic prismatic, "a"=5.126 A,± .01 "b"=8.880 A ± .007, "c"=7.619 A ± .006; β =133° 37' ± 8' . Absent spectra, (h0l) when h is odd, (0k0) when k is odd. Space group C_{2h}^5,($P2_1/a$). Two molecules per unit cell. Molecular symmetry, centre. Volume of unit cell, 249.6 A^3. Absorption coefficient for X-rays,

(λ = 1.54 A.), μ = 14.25 cms.$^{-1}$. total number of electrons in the unit cell = F(ooo) = 124

The lattice constants have been redetermined since previously reported structures, by means of carefully calibrated moving film photographs. This was done by superimposing sodium chloride powder lines on the moving film records, taken about the necessary axes. Extreme care was taken to see that both the sodium chloride powder sample and the crystal were very accurately set in the centre of the camera. Since the sodium chloride lattice constants are known very accurately, the film can be calibrated for $2\sin\theta$ values, and all errors due to variations in the camera radius eliminated.

Experimental Measurements :-

1) Preparation of Crystals:-

Crystals of succinic acid when grown from water, give needles developed along the "c" axis. These crystals show very pronounced cleavage along this axis. When grown from ethyl acetate the "a" axis is usually developed, and again the cleavage is along the "c" axis.

No difficulty was experienced in obtaining single crystals of suitable size and shape for the "a" and "c" axis rotation photographs. In the case of the "b" axis however , crystals of suitable shape were found to be almost invariably twinned, and consequently useless.

Owing to the brittleness of the crystals it was exremely difficult to cleave a suitably shaped piece from a large crystal, and it was only after many attempts that suitable crystals were obtained.

Crystals of succinic acid are relatively perfect and give very sharp reflections. In order to prevent any primary extinction of the diffracted beams, which would cause errors in the structure factor measurements, all the crystals were immersed in liquid air before being photographed. This made no apparent external difference to the crystals but it was hoped that the thermal shock would increase their mosaic character.

2) Intensity Measurements and Corrections :-

In this work it was necessary to make a complete survey of all the reflections within the range of copper K_α radiation (λ = 1.54 A). This was carried out by photographic methods, using small crystals completely immersed in a uniform X-ray beam. The photographic surveys were made by moving film methods, on an instrument of the equi-inclination Weissenberg type. The $2\sin\theta$ values for all the possible 585 planes which could reflect using copper K_α radiation were calculated and it was found that measurable intensities could be obtained for 455 of these. This represents nearly 80% of the total, the others being too weak to give reflections which would record on the films.

It was found that all the reflections could be obtained on the accessable layer lines of the rotations about the (100), (010), (001) and (101), axes. The layer lines recorded, with the dimensions used are given in table 3.

Table 3.

The layer lines recorded and the cross section of the crystal used, in m.m.

Layer Line	Crystal Size.
0kl	
1kl	.09 × .11 & .45 × .52
2kl	
3kl	
h0l	
h1l	
h2l	.14 × .16
h3l	
h4l	
h5l	
hk0	
hk1	
hk2	.23 × .26
hk3	
hk4	

Layer Line.	Crystal Size.
$h0\bar{h}$	
$h0\overline{h\pm1}$	
$h0\overline{h\pm2}$	.38 × .42
$h0\overline{h\pm3}$	

As can be seen from the above table, two different crystals were used for the "a" axis reflections. This was found to increase the range of intensity which could be accurately measured, the small crystal being used for the strong reflections , and the large crystal for the weak reflections. In the case of the other zones instead of using two crystals, two series of films were taken with long and short exposure times. The intensities of the strong reflections were measured on the short series, and the weak on the long.

The intensities were measured by the method of visual estimation. The multiple film technique (Robertson, 1943.) was employed, using Kodak Industrex Type D X-ray film, and an accurately measured film to film reduction factor. In the great majority of cases, two or even three measurements were made of the intensity of any given plane , due to its occurence in different zones. Each intensity was also estimated separately by two different observers, consequently it can be assumed that random errors have been eliminated in these measurements.

It can be seen from table 3 that the crystal specimens were quite uniform in cross-section, and no correction was applied

to the observed intensities for the absorption of the X- ray beam in the crystal. The normal Lorentz and polarisation factor were employed and also a geometric rotation correction for all reflections on layer lines other than zero. This correction is to allow for the angular velocity of rotation of the planes through the reflecting angle, and the factors described by Tunell (1939) were used.

3) Correlation of Structure Factors :-

As the intensities of planes in different zones are independently measured on different series of films, the observed structure factor values which are obtained from them are not all on the same relative scale. The structure factor values must be correlated , and this is done by making use of the reflections which are common to two or more zones. There is very little precedent for this type of work and in an endeavour to find the best method, two entirely different procedures were adopted, these are as follows,

a) Some reflections occuring on the zero layer of the (101) also appear on the (0kl), (1kl), (2kl), and (3kl), zones. By comparing these zero layer (101) reflections to the same reflections on the "a" axis layers, factors can be found which will put (0kl), (1kl), (2kl), and (3kl), planes all on the same scale. The $1^{st.}$, $2^{nd.}$ and $3^{rd.}$ layer lines of the (101) axis also have some reflections which appear on all the "a" axis zones. Hence by comparing each of the diagonal layer lines in turn with (0kl), (1kl), (2kl), and (3kl), several estimates can be made of the factors needed to

correlate the "a" axis layers with each other. This method ensured that the various zones of the "a" axis layers were accurately scaled, since in effect the same factors were estimated several times, once for each of the (101) layers.

The (0kl), (1kl), (2kl), and (3kl), reflections were then used as a standard for all the reflections appearing on the other zones. For example the planes common to (h1l) zone and any of the "a" axis layers were then used to correlate the (h1l) zone with (0kl), (1kl), (2kl), and (3kl). This was done for each of the observed zones in turn, so that for each, a numerical factor was obtained which could be used to bring it to the common "a" axis scale.

b). The second method was much more straightforward, and makes use of intensities estimated on oscillation photographs. On any oscillation photograph about an axis, reflections on all the accessible layer lines are recorded. If the intensities of these reflections are estimated on the oscillation film by the multiple film technique (Robertson, 1943), they are all obtained on the same relative scale. These same reflections will however occur on the moving film records on different layer lines of the axis, and they can be used to bring all the different layer line measurements to the same scale. In the present case the "a" axis reflections were all put on the same scale by this method. Every other zone was then compared to the (1kl) zone, and consequently all theobserved structure factors correlated.

It was found that by using these two methods independently,

that they gave comparable results. From this it was concluded that both methods are reliable. Method (a) employs more common planes, and consequently the results should be more accurate, the second method on the other hand is simple and lends itself more to easy tabulation , which is quite an important factor when a large mass of experimental data has to be dealt with. In general, three dimensional investigations can be made much less tedious if efficient methods of tabulation can be devised for the various stages of the procedure.

When the correlation of observed structure factors had been carried out, it was found that the discrepancy between the F's measured on different zones was of the order of 10%. This was rather more than can be accounted for by the known deviation in the visual estimates of the intensities. The technique employed which gives an accuracy of about 10% in the observed intensity value would be expected to give F values correct to about 5% . The same order of agreement was obtained in other recent three dimensional investigations on Naphthalene (Abrahams, Robertson, and White, 1949) and on Anthracene (Robertson, Sinclair, and Mathieson, 1950.), and it consequently must be assumed that in general the accuracy of the F measured values is of the order of 10%. This may not be equally true of the data usually employed in two dimensional investigations. In this case only F values for planes in principal zones are used , and the intensities are not subject to the errors which may arise with general hkl reflections,

such as insufficient correction for absorption, or for the angular velocity of rotation of the plane.

It should be noted that although the correlation described above put all the measured structure factors on the same relative scale, it did not put them on an absolute scale. This was done after the determination of the calculated structure factor values, and the method will be described later when the atomic scattering curve is being considered.

4.) Determination of Phase Constants :-

The structure factor equation for the space group $P2_1/a$ is as follows,

$A = +4\cos 2\pi(hx + lz) \cos 2\pi ky$ when h + k is even.

$A = -4\sin 2\pi(hx + lz) \sin 2\pi ky$ when h + k is odd.

Where A is the contribution of each atom of the asymmetric unit to any plane hkl.

Using these equations, structure factors were calculated and the phase constants for the observed structure factors obtained in the usual way. The calculated values for the structure factors were determined using the atomic co-ordinates previously reported as the result of the double Fourier series investigation of the acid(Morrison and Robertson, 1949.). From this structure reasonably certain signs were obtained for 442 of the planes, and the remaining 13 had all geometric structure factor values less than 2% of the possible theoretical maximum. These latter had all

to be excluded from the final summation, as they were assumed to be unreliable.

5.) Atomic Scattering Curve :-

The molecule of succinic acid consists mainly of carbon and oxygen atoms, and theoretically each type of atom should require a different atomic scattering correction. However the atomic numbers of these two atoms are sufficiently close to justify the use of an average atomic scattering curve. This was used in conjunction with allowing for the greater scattering power of the oxygen atoms by multiplying their contribution to any plane by a numerical factor. This factor is theoretically equal to the number of electrons in the oxygen atom divided by the number in the carbon atom.

The curve itself was derived experimentally, making use of the full three dimensional data which was available. Since this curve is deduced empirically from the observed results, it already incorporates any temperature modification which may be necessary, consequently no further correction was made for this factor.

The figures required to reproduce this curve are given in table 4.

Table 4.

Atomic Scattering Curve.

$\sin\theta$ (λ=1.54A)....	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
f	100.0	72.0	54.0	42.5	32.4	25.0	18.5	14.4	11.0	8.5

The calculated structure factor values were put on to an absolute scale by adjusting the maximum of the experimental scattering curve to the theoretical maximum, in accordance with the known relationship

$$F_{ooo} = S_{ooo} \times f_{ooo}$$

where,

F_{ooo} = Total No. of electrons in unit cell.

S_{ooo} = The maximum value of the structure amplitude.

f_{ooo} = Required theoretical maximum of scattering curve.

The observed structure factor values were then put on to an absolute scale by bringing them to the same scale as the calculated values.

At this stage in the investigation it was found that agreement between the observed and calculated values of the structure factors, expressed in the usual manner as,

$$\text{Discrep.}\Delta = \frac{\sum\left(|F_{obs.}| - |F_{calc.}|\right)}{\sum |F_{obs.}|} \times 100$$

was approximately 23%. As this only represents an increase of 1% from the value obtained for the two dimensional data, it was considered to be sufficiently good to proceed to the final three dimensional Fourier synthesis, and the ultimate refinement of the structure.

It is possible that the above discrepancy would have been even better if two separate atomic scattering curves had been used, one for each of the two types of atom. It is not however practical to do this with very great accuracy, as experimental scattering curves are better to be estimated from a large number of planes, and thereis not a large number of planes available whose observed intensity is due solely to either carbon or oxygen atoms.

Fourier Synthesis :-

The observed structure factors "F" when they have been put on an absolute scale and their phase constants determined, are ready to be used as the coefficients in the Fourier series. Before doing this they are converted to the quantity "F'", such that,

$$F'_{hkl} = F_{hkl} \times \frac{1000}{V}$$

where V= volume of the unit cell.

This gives the final totals after summation in the form of electron densities per $A^3 \times 1000$. It is usual with the two dimensional Fourier method to have the final totals in the form of electron densities per $A^2 \times 100$, but by having the 1000 factor in the case of the three dimensional investigation, additional accuracy is obtained. As three figure methods were used throughout the summation and numerical work, with rounding off deferred to the last stage, the final totals were consequently tabulated to three significant figures.

For the evaluation of the electron density, the crystal axis "a" was subdivided into 30 parts, while the "b" and "c" axes were each subdivided into 60 parts. This gave the following intervals along each axis.

$1/30^{th.}$ of "a" = 0.1709 A

$1/60^{th.}$ of "b" = 0.1480 A

$1/60^{th.}$ of "c" = 0.1269 A

The quarter of the unit cell which constitutes the asymmetric crystal unit was then covered by extending the summation over $15/30^{ths.}$ of "a", $30/60^{ths.}$ of "b" and $60/60^{ths.}$ of "c".

The general expression for the electron density ρ at any point (xyz) is

$$\rho_{(xyz)} = \frac{1}{V}\sum_{-\infty}^{+\infty}\sum\sum\sum F_{(xyz)} \cos 2\pi (hx + ky + lz)$$

where V= volume of the unit cell, and x, y, and z, are the co-ordinates expressed as fractions of the axial length.

In the case of succinic acid this series would have 455 terms if all the structure factors were included in the summation. In actual fact only 442 terms were used, the other 13 being those whose phase constants were in doubt. The 13 omitted planes all had very small amplitudes and even their combined effect on the final summation totals would have been insignificant. If any coefficient is included in the series with the wrong sign, the resulting error would be twice as significant as the error resulting from its complete omission, This was considered to be sufficient justification for including only 442 of the possible 455 terms.

To evaluate the full triple Fourier series entails a very large amount of mechanical labour. If the summation had been done in the same fashion and on the same machines as are usually employed for the Fourier projection method, it is conceivable that the work would have taken well over a year of constant work on the adding machine. In view of this fact the Hollerith punched card system was used and the work was done by the Scientific Computing Service Ltd. of 23 Bedford Square, London. The summation was carried out on a Hollerith International business machine, which employs the punched card system. In this case the position of the punched holes in the cards would correspond to the magnitude and phase of the Fourier term.

The general Fourier expression may be reduced to the form,

$$\rho(xyz) = \frac{4}{V}\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty}\Big\{\Big[F(hkl) + F(\overline{hkl})\Big]\cos 2\pi hx \cos 2\pi ky \cos 2\pi lz + \Big[F(hk\bar{l}) - F(hkl)\Big] \sin 2\pi hx \sin 2\pi ky \sin 2\pi lz \quad (\text{for } h+k \text{ even})$$

$$- \Big[F(hkl) + F(hk\bar{l})\Big] \sin 2\pi hx \sin 2\pi ky \sin 2\pi lz + \Big[F(h\bar{k}l) - F(hkl)\Big] \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz \Big\} \quad (\text{for } h+k \text{ odd})$$

The above form is the one most suitable for the Hollerith machines.

The multiplicities of the various terms which are used in the Fourier series are as follows

$F(hkl)$ 4 if $F(hk\bar{l})$ is given

$F(0kl)$ 4 if $F(0k\bar{l})$ is not given

$F(hk0)$ 4

$F(h0l)$ 2 if $F(h0\bar{l})$ is given

$F(0k0)$ 2

$F(00l)$ 2 if $F(00\bar{l})$ is not given

$F(h00)$ 2

$F(000)$ 1

Hence by considering the above multiplicities, the various sums and differences of planes with "l" positive and "l" negative which are introduced into the Fourier expression are obtained from all values of "l" as follows

	h even	h odd
For k = 0	$2[F(h0l) + F(h0\bar{l})]$	
	$2[F(h0\bar{l}) - F(h0l)]$	
For k > 0	$4[F(hkl) + F(hk\bar{l})]$	$-4[F(hkl) + F(hk\bar{l})]$
and even	$4[F(hk\bar{l}) - F(hkl)]$	$4[F(hk\bar{l}) - F(hkl)]$
	$2[F(0k0)]$	
For k > 0	$-4[F(hkl) + F(hk\bar{l})]$	$4[F(hkl) + F(hk\bar{l})]$
and odd	$-4[F(hk\bar{l}) - F(hkl)]$	$4[F(hk\bar{l}) - F(hkl)]$

Using the above combinations the observed coefficients are combined among themselves to give new coefficients, from which

the first set of Hollerith cards are punched. These cards contain the magnitude and sign of the coefficient together with its (hkl) index. The machine then records the function,

$$\sum h \begin{bmatrix} \cos \\ \sin \end{bmatrix} 2\pi hx$$

for the given range of "x", the values obtained being used for the new coefficients to extend the summation over the other two axes.

When the complete evaluation had been done the results which represented the electron density at 27,000 points in the asymmetric unit, were sent back from the Scientific Computing Service Ltd. in the form of printed sheets.

Graphical Representation :-

In the normal Fourier projection method the electron density at a series of points on the base of the asymmetric unit is the result of the synthesis. This is usually completely drawn out, by the usual method of plotting the variation of electron density along one axis at constant levels of the other. In the case however of the triple summation , the results are in the form of electron densities at a series of points in space, and as most of this represents parts of the asymmetric crystal unit where there is no great density of scattering material, there is no necessity to perform the very tedious task of representing graphically all the information provided as a result of the synthesis. Instead use is made of the fact that the positions of the

atoms are known approximately, and cross sections of the asymmetric unit near to the atomic centres are represented graphically.

The general background of electron density in the regions between the molecules was very uniform, and seldom greater than just above zero, with occasional negative regions which never exceeded $-0.5\ eA^{-3}$. This showed that the observed structure factors had been scaled correctly, before the summation.

For each atom of the asymmetric unit, the electron density was plotted on eight sections, chosen so that four were parallel to the (010) axis and four parallel to the (001). To do this about 600 graphs of the electron density had to be drawn so that for any given section or level, of say constant "y", the variation of electron density along "z" for example, could be plotted for various increments of "x". The horizontal scale was chosen so that 10 cms. represented 1A, and the vertical scale so that 1 cm. represented $0.5\ eA^{-3}$. On these graphs the positions of the electron contour levels on the horizontal scale, were marked for every increment of $0.5\ eA^{-3}$.

From the electron density plot, the atomic centres were estimated visually. The co-ordinates being obtained in terms of the nearest cell division, so that only a small direct measurement had to be made. It was possible to make four separate measurements for each parameter, which should eliminate any random error. With the scale of 10 cms. = 1 A a direct measurement of 1 m.m.

represented 0.01 A and the centres could be easily fixed with an accuracy of 1 m.m.

The results of the measurements on the sections is shown on Table 5. and Figs. 12 and 13 show two sections through each atom, near to the centre of the atom.

Table 5.

Co-ordinates estimated from Crystal Sections.

Monoclinic crystal axes, centre of symmetry as origin, "x" and "z" are obtained from the sections parallel to (010), and "y" from the sections parallel to (001), at levels along the "b" and "c" axes as indicated.

Atom. [cf. fig 14.]	Level of Sections. b/60	c/60	xA.	yA.	zA.
C_1	5	6	0.2647	0.5710	0.6049.
	4	5	0.2697	0.5730	0.6049
	3	4	0.2696	0.5720	0.6069
	2	3	0.2736	0.5710	0.6049
C_2	4	17	0.1379	0.3100	1.9777
	3	16	0.1369	0.3120	1.9737
	2	15	0.1359	0.3110	1.9777
	1	14	0.1229*	0.3080	1.9647*

Table 5. (cont.)

Atom.	Level of Sections b/60	c/60	xA.	yA.	zA.
O_1	-6	14	-0.6165	-0.6950	1.9537
	-5	15	-0.6245	-0.6930	1.9497
	-4	16	-0.6275	-0.6970	1.9487
	-3	17	-0.6535*	-0.6950	1.9257*
O_2	10	27	0.8464	1.2260	3.2175
	9	26	0.8504	1.2300	3.2185
	8	25	0.8544	1.2400	3.2205
	7	24	0.8664*	1.2400	3.2415*

* Omitted from average, sections elliptical.

It can be seen from an inspection of table 5. that the co-ordinates are obtained with a high degree of precision, although the electron density distribution in the regions of the atom is not truely spherical. Examination of figs. 12, and 13, shows that the carbon atoms are much more nearly spherical than the oxygen atoms, and that the sections parallel to (001) through the oxygen atoms are much more circular than the sections parallel to the (010) axis. This suggests that the oxygen atoms are elongated

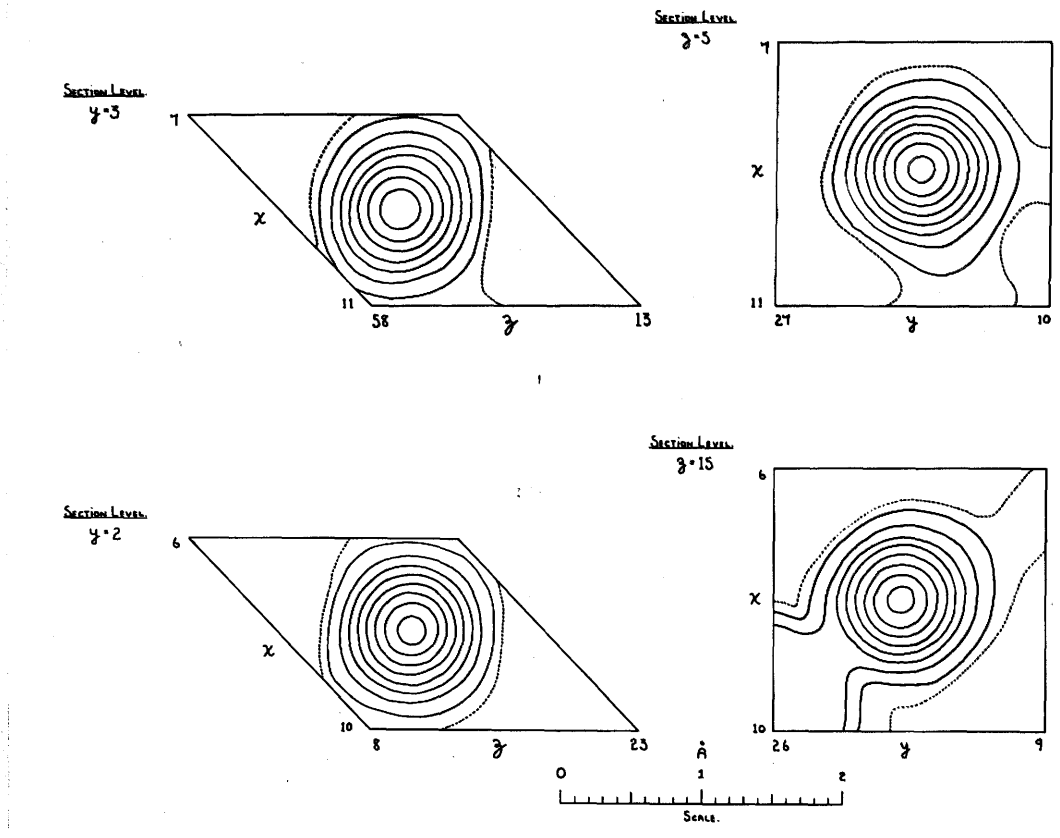


Fig. 12.

Crystal sections parallel to (010) and (001) drawn near to the centres of each of the two carbon atoms of the asymmetric unit. Each contour line represents a density increment of 1 eA^{-3}, the outside dotted line being the $\frac{1}{2}$ electron line. Co-ordinates are given in 30 of "x" and 60 of "y" and "z".

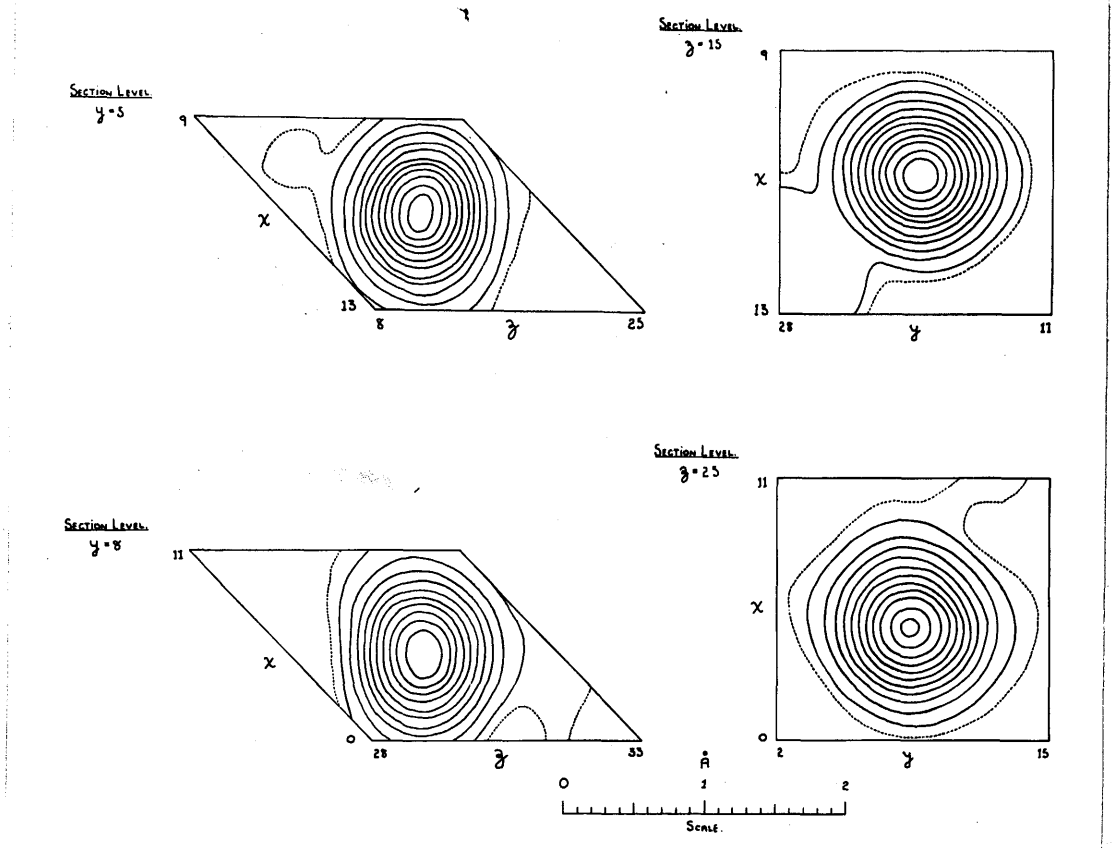


Fig. 13.

Crystal sections parallel to (010) and (001) drawn near to the centres of each of the two oxygen atoms of the asymmetric unit. Each contour line represents a density increment of 1 eA^{-3}, the outside dotted line being the $\frac{1}{2}$ electron line. Co-ordinates are given in 30 of "x" and 60 of "y" and "z".

in a direction approximately at right angles to the "y" axis of the cell. The fact that only a few of the sections show pronounced ellipticity probably indicates that the effect actually represents a physical reality, and is not due to any unsuspected error in the observed intensity estimates

As a result of the non-spherical distribution, the co-ordinates as measured in some cases show a pronounced drift from what must be considered the true atomic centres. These sections are marked with an asterisk in table 5. It can be seen that as a result of this drift there is a source of error introduced into the three dimensional method of investigation which is not encountered in the projection method. If the sections used in the three dimensional method were chosen carelessly, a good two dimensional projection analyses may, in fact, give better co-ordinates. In the present investigation using eight sections for each atom, and arranging them near to, and on each side of, the true atomic centre, any progressive error due to a small drift will be eliminated when the co-ordinates from each of the sections are averaged.

In the case of carbon atom C_1 four sections were also taken parallel to the (100) axis, to give a further check on the co-ordinates and on the spherical distribution of the atom. It was apparent from these sections that the carbon atoms were indeed nearly truely spherical, and as the co-ordinates obtained agreed well with those from the sections in the other two directions,

it was decided that it was not necessary to repeat these sections parallel to the (100) axis for the other atoms of the asymmetric unit.

Table 6. gives the average values found for the atomic co-ordinates, estimated from the measurements on all the sections.

Table, 6.

Co-ordinates measured from sections. "x", "y", "z", referred to monoclinic axes, with centre of symmetry as origin, and "x'", "y", "z'" are orthogonal co-ordinates referred to the "a" and "b" crystal axes and their perpendicular "c'".

Atom. (cf. fig.14.)	x A.	y A.	z A.
C1.	0.2694 ± .005	0.5710 ± .003	0.6054 ± .0015
C2.	0.1369 ± .001	0.3102 ± .002	1.9763 ± .003
O1.	-0.6228 ± .006	-0.6950 ± .002	1.9507 ± .003
O2.	0.8504 ± .004	1.2340 ± .008	3.2188 ± .002

Atom. (cf. fig.14)	x'A.	z'A.
C1.	-0.1482	0.4383
C2.	-1.2264	1.4308
O1.	-1.9684	1.4123
O2.	-1.3699	2.3304

Table 6.(cont.)

Atom. (cf.fig.14.)	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
C1.	18.9199	23.1483	28.6052
C2.	9.6145	12.5755	93.3802
O1.	-43.7392	-28.1753	92.1706
O2.	59.7236	50.0264	152.0883

All the figures in the above table have been quoted to four places of decimals , but it is not suggested that this by any means represents the accuracy that is claimed for the results. Throughout the numerical work on the measurements of the sections, four figure accuracy was maintained, and the figures in table 6. have been quoted as they were calculated, with rounding off deferred.

It is difficult to judge the absolute accuracy of the method of investigation , but it is known that random errors in the observed structure factor values have very little effect on the position of the atomic centres. The Fourier series used is also known to be very extensive, and the number of terms which may have been included with the wrong or doubtful sign is almost negligible in comparison to the others. It can be seen from the table, that the atomic centres can in general be assigned to a position which is reproducible to .005 A , so taking all these factors into consideration , it is estimated that the co-ordinates should

be accurate to better than .01A, with the consequent estimated error in the bond lengths of the molecule, not much exceeding this figure of .01A.

The shift in atomic co-ordinates due to the Fourier synthesis was not very great, it can best be appreciated when seen in tabular form, as in Table 7.

Table, 7.

Comparison of the atomic co-ordinates, referred to the monoclinic axes, obtained from the present investigation and those reported previously by Morrison and Robertson, (1949).

Atom. (cf.fig.14.)	xA. Present	xA. Previous	xA. Shift	yA. Present	yA. Previous	yA. Shift
C1 .	.269	.276	.007	.571	.592	.021
C2.	.137	.099	.038	.310	.326	.016
O1.	- .623	- .602	.021	- .695	- .703	.008
O2.	.850	.864	.014	1.234	1.233	.001

Atom. (cf.fig.14.)	zA. Present	zA. Previous	zA. Shift
C1.	.605	.602	.003
C2.	1.976	1.966	.010
O1.	1.951	1.976	.025
O2.	3.219	3.234	.015

Molecular Dimensions :-

The dimensions of the succinic acid molecule calculated from the atomic co-ordinates measured on the sections, are shown in fig.14.

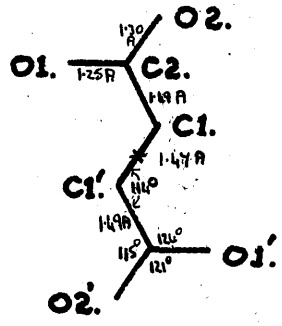


Fig. 14.

Dimensions of the Molecules.

Table, 8.

Present results for the molecular dimensions compared to the previous results obtained by Morrison and Robertson(1949).

	Present.	Previous.
C1'---C1.	1.470 ± .01	1.50 ± .02
C1 ---C2.	1.489 ± .01	1.51 ± .02
C2 ---O1.	1.251 ± .01	1.25 ± .02
C2 ---O2.	1.297 ± .01	1.30 ± .02

Table,8.(cont)

	Present.	Previous.
C1'—C1 —C2.	114° 3'	112°
C1 —C2 —O1.	124° 3'	124°
C1 —C2 —O2.	114° 37'	114°
O1 —C2 —O2.	120° 55'	122°

The other crystal distances which can be calculated when the co-ordinates of the atoms have been estimated, have not as yet been determined, since it is intended to do a further check on the atomic co-ordinates before final values are reported. This check consists of representing graphically the electron density in two planes, which define the molecule. This will be fully described in the following para graphs.

Sections Through the Planes of the Carbon and Oxygen Atoms of the Molecule :-

By considering the molecular and space group symmetry, it is obvious that the four carbon atoms which represent the chain of the molecule, must all lie on a plane which passes through the origin of the unit cell. Similarly the four oxygen atoms joined by the hydrogen Bonds are also situated about a centre of symmetry, and must also be co-planar. This plane of the carboxyl groups also passes through a centre of symmetry which is situated between adjoining molecules. Morrison and Robertson

have shown that these two planes make an angle of approximately 9^{o} with one another.

If the electron density on these two planes is represented graphically, then the various bond lengths and angles of the molecule can be measured directly from the resulting density diagram. This can be done in the following manner.

The equation of the planes of the carbon atoms , when referred to rectangular axes , was found to be,

$$x' = 0.47794\ y - 0.96075\ z'$$

when referred to monoclinic axes,

$$x = 0.47794\ y - 0.00578\ z$$

The equation cannot be used in the above form, but if "x" is expressed in $30^{ths.}$ and "y" and "z" in $60^{ths.}$ the equation can be written as,

$$x = 0.414\ ny - 0.0043\ mz$$

where "n" and "m" can be any value of $60^{ths.}$ of "y" and "z".

As the plane defined above does not coincide with any simple crystallographic position, its places of intersection with the "x" axis must be calculated by substitution, for an array of values of "n" and "m". The electron density in the section can then be evaluated by further graphical interpolation from the summation totals. From the array of densities obtained, a contour map can be drawn showing the electron distribution in the plane. To draw this map its boundry lines must be known . They are "d" the intersection of the plane with plane $z' = 0$, and "e" the intersection of the plane with plane $y = 0$

Substituting in the equation of the carbon plane, we get, when $z' = 0$,

$$x' = .47794\ y$$

and hence, the angle between the "b" crystal axis and "d" is

$$\tan^{-1} .47794 = 25^{\circ}33'$$

when $y = 0$,

$$x' = -.96075\ z'$$

and similarly, the angle between "c'" and "e" is

$$\tan^{-1}(-.96075) = -43^{\circ}51'$$

Also the lengths of the lines"d" and "e" are

$$d = b/\cos 25^{\circ}33' = 9.8425 \quad \text{(Interval } d/60 = .16404)$$

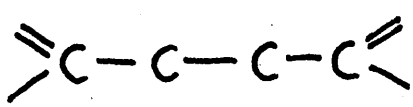
$$e = c'/\cos 43^{\circ}51' = 7.6487 \quad \text{(Interval } e/60 = .12748)$$

The angle between "d" and "e" can then easily be calculated, using the above information.

The above procedure which can be used to plot the electron density on any plane through the crystal, was also employed to investigate the plane of the carboxyl groups. This work has not as yet been completed and the final results cannot be given.

Discussion :-

Although the investigation has not as yet been completed, the new atomic co-ordinates have been obtained. The difference between these and the two dimensional co-ordinates of Morrison and Robertson, (1949) is never greater than .04A and seldom greater than .02A. The effect of these changes on the molecular dimensions is very interesting, and definitely confirms that the C----C bonds are not normal single bonds. As mentioned in the introduction, the shortening of the centre C----C bond in structures of type,



had previously been detected in geranylamine hydrochloride and dibenzyl (Jeffrey 1947, Cox and Cruickshank 1948.), but never has the effect been so large as that now found with succinic acid.

The work of Morrison and Robertson (1949) on the dicarboxylic acids, succinic, adipic, and sebacic, has suggested that the presence of the carboxylic groups at the end of the chain, cause an alternation in the C----C bond lengths of the chain.

Although the differences in bond length were always just on the limits of experimental error, the occurrence of the effect in several acids seemed to indicate that it was real.

The present work on succinic acid has shown that the carboxyl groups have a very definite effect on both the C----C links of the chain, and especially on the central bond. In view of the fact that the contractions from the normal single bond length of 1.54 A are obviously significant, and that even the difference of .02 A between the two C----C bond of the chain, is outside experimental error. It would appear that the contractions previously measured in the other acids are also significant.

Binnie and Robertson (1949) reported that the carbon chain of the molecule of hexamethylene diamine dihydrochloride, may also have alternations in the C----C bond lengths. Again the differences were just on the limits of experimental error , and no definite conclusions could be drawn, but it seems probable that the effect was similar to that noticed with the acids. If this is the case the alternation can apparently be caused by a variety of different functional groups at the end of the chain.

It is of interest and probably of importance to note, that in the one acid of the series with an odd number of carbon atoms in the molecule, which has been done accurately, i.e. Glutaric acid (Morrison and Robertson, 1949.), no contractions have been noticed.

The presence of the hydrogen atoms of the molecule has not as yet been detected. This is not surprising since the sections drawn were positioned arbitarly with respect to them. It is probable that there may be some indication of their position when the planes through the various parts of the molecule are drawn. If necessary special sections can be drawn through the calculated positions of the hydrogen atoms, and this will definitely determine whether or not they have been resolved by the Fourier synthesis.

APPENDIX.

A NOTE ON THE CRYSTAL STRUCTURE OF AZELAIC ACID.

Azelaic acid $C_9H_{16}O_4$, is a member of the series of aliphatic acids with an odd number of carbon atoms. Previous measurements of the unit cell and space group have been reported by Caspari (1928, 1929.) for two different crystal modifications of the acid. The unit cell and space group of one of these modifications has been redetermined as a preliminary to the complete investigation of the molecule, which will be done later.

The experimental work on this one modification of the acid is now complete, and is briefly reported in the following paragraphs.

Preparation of Crystals :-

Ethyl acetate was found to be the best solvent for the acid, giving suitable crystals on slow evaporation. The acid was on the whole difficult to crystallise, as in most solvents it had a high surface activity and tended to come out of solution by creeping up the sides of the containing vessel. Large crystals could be grown from saturated ethyl acetate solutions by nucleating the crystallisation with a small crystal suspended in the solution on the end of a platinum wire.

The crystals never tended to grow as needles, and were

either flat chunky plates or squat prisms. Crystals of all sizes were obtained, and the great majority of them were found to be twinned about the "a" axis. The cleavage plane of the crystal was along an axis which was subsequently found to be a diagonal of the cell which was chosen.

Crystal Data :-

Azelaic acid, $C_9H_{16}O_4$; M, = 188.25 ; m.p. 106.5° ; d, calc. 1.252 , found 1.230. Monoclinic prismatic, "a" = 5.49 ± .06A "b" = 9.45 ± .05A, "c" = 18.99 ± .07A, $\beta = 97°$. Absent spectra, (0k0) when k is odd, (h0l) when l is odd. Space group ($P2_1/c$), C_{2h}^5. Four molecules per unit cell; molecular symmetry, none. Volume of unit cell 977.8 A^3 ; Total number of electrons per unit cell = F(000) = 408.

Space group : This was determined uniquely when the absences considered above were verified. It should be reported however, that one weak reflection was found in a position corresponding to the (030) plane, which is forbidden by the symmetry of $P2_1/c$. This would suggest that the space group may be P2/c, but it was not found possible to arrange four asymmetric molecules in this arrangement, and it was decided that the weak (030) reflection must be due to some harmonic of the copper K_α radiation, which was being produced by the X-ray tube in small quantities.

X-ray Measurements :-

All the X-ray work was carried out with copper K_α radiation (λ =1.54A) and photographic methods. The cell

dimensions, space group etc., were determined from rotation and moving film photographs, while the intensity measurements were obtained exclusively from moving film photographs. The intensities for planes in two zones of the crystal, the (0kl) and (h0l) were obtained using the multiple film technique (Robertson, 1943.) and the structure factors were derived by the usual formulae for mosaic type crystals.

Position of Molecules in the Unit Cell :-

The asymmetric crystal unit consists of one molecule, and if the molecule has a two-fold axis as would be expected from its similarity to glutaric acid (Morrison and Robertson, 1949) it does not appear to use this symmetry in the unit cell. The $(10\bar{4})$ plane is very strong and indicates that the plane of the carbon chain possibly lies in this plane. If this is the case the centre carbon atom of the chain will probably lie on the two-fold screw axis of the space group, with the two-fold axis of the molecule if it has one, at an angle to this screw axis. The plane of the carbon chain of the molecule would then be normal to the "ac" face of the cell, and at an angle of about 43° to the "bc" face of the cell. The carboxyl groups of end to end molecules will probably form hydrogen bridges across the centres of symmetry between them, with the plane of these carboxyl groups making some small angle with the plane of the carbon chain.

The (021) plane is also very strong, which indicates

that the molecule is probably tilted so that the line joining the mid-points of the C----C bonds of the chain, is parallel to this plane. This would mean that the molecule is tilted at approximately 14° to the "ac" face of the cell.

Assuming that the molecular dimensions were similar to glutaric acid (Morrison and Robertson, 1949.), and that the molecule was situated in the cell as suggested above, structure factors were calculated. These were found to give a rough interpretation of the observed intensities, but not sufficiently good to further refine the structure of the molecule by the Fourier method.

Remarks :-

Caspari (1929) reported that he found two definite crystal modifications of the acid, which he called the α and the β forms. Although no evidence was found for two crystalline modifications during this present investigation, polymorphism is common among this series of acids. The unit cell measurements reported by Caspari were as follows,

β Azelaic acid, "a"=5.61 A, "b"=9.58 A, "c"=27.2 A, $\beta = 136^{\circ}30'$

α Azelaic acid, "a"=9.72 A, "b"=4.83 A, "c"=27.1 A, $\beta = 129^{\circ}31'$

The crystal modification studied in this investigation was obviously the same as Caspari's β modification, but with a different choice of "c" axis. The justification for this choice lies solely in the length of the axis, since the ultimate aim of the investigation is accurate measurements of the inter-atomic

distances, the shorter 18.99 A axis is preferable to one which is 27.2 A long.

The crystal modification which Caspari called the α form, shows obvious similarities to the measurements given by Morrison and Robertson (1949) for glutaric acid, the only difference being the expected increase in the length of the "c" axis to accomodate the increased chain length.

β Glutaric acid, "a"=10.06 A, "b"=4.87 A, "c"=17.40 A, β =132.6°

α Azelaic acid, "a"= 9.72 A, "b"=4.83 A, "c"=27.14 A, β =129°31'

It has been the recent custom to designate the modification stable at room temperatures, as the β acid. In the case of azelaic acid however, both forms seem to be stable under nearly similar conditions.

It can be seen from the above remarks that it would be preferable to study the crystal form of azelaic acid which Caspari called the α modification, since this would mean that all the results would be directly comparable to the previous accurate work which has been done on these odd carbon acids. The difficulty however seems to be getting crystals of the so called α form of the acid. Numerous crystallisations under very different conditions and using different solvents, gave only the one form in this present investigation.

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